

## Methods of calculation

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### Pauling electronegativity

Pauling first proposed<sup>[2]</sup> the concept of electronegativity in 1932 as an explanation of the fact that the covalent bond between two different atoms (A–B) is stronger than would be expected by taking the average of the strengths of the A–A and B–B bonds. According to valence bond theory, of which Pauling was a notable proponent, this "additional stabilization" of the heteronuclear bond is due to the contribution of ionic canonical forms to the bonding.

The difference in electronegativity between atoms A and B is given by:

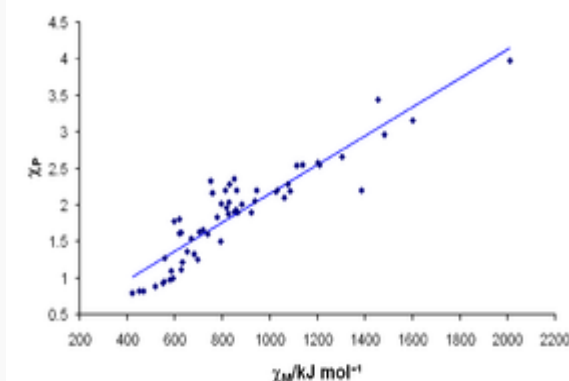
$$\chi_A - \chi_B = (\text{eV})^{-1/2} \sqrt{E_d(\text{AB}) - [E_d(\text{AA}) + E_d(\text{BB})]/2}$$

where the dissociation energies,  $E_d$ , of the A–B, A–A and B–B bonds are expressed in electronvolts, the factor  $(\text{eV})^{-1/2}$  being included to ensure a dimensionless result. Hence, the difference in Pauling electronegativity between hydrogen and bromine is 0.73 (dissociation energies: H–Br, 3.79 eV; H–H, 4.52 eV; Br–Br 2.00 eV)

As only differences in electronegativity are defined, it is necessary to choose an arbitrary reference point in order to construct a scale. Hydrogen was chosen as the reference, as it forms covalent bonds with a large variety of elements: its electronegativity was fixed first<sup>[2]</sup> at 2.1, later revised<sup>[5]</sup> to 2.20. It is also necessary to decide which of the two elements is the more electronegative (equivalent to choosing one of the two possible signs for the square root). This is done by "chemical intuition": in the above example, hydrogen bromide dissolves in water to form  $\text{H}^+$  and  $\text{Br}^-$  ions, so it may be assumed that bromine is more electronegative than hydrogen.

To calculate Pauling electronegativity for an element, it is necessary to have data on the dissociation energies of at least two types of covalent bond formed by that element. Allred updated Pauling's original values in 1961 to take account of the greater availability of thermodynamic data,<sup>[5]</sup> and it is these "revised Pauling" values of the electronegativity which are most usually used.

## Mulliken electronegativity



The correlation between Mulliken electronegativities ( $\chi$ -axis, in kJ/mol) and Pauling electronegativities ( $\chi_P$ -axis).

Mulliken proposed that the arithmetic mean of the first ionization energy and the electron affinity should be a measure of the tendency of an atom to attract electrons.<sup>[6][7]</sup> As this definition is not dependent on an arbitrary relative scale, it has also been termed **absolute electronegativity**,<sup>[8]</sup> with the units of kilojoules per mole or electronvolts.

However, it is more usual to use a linear transformation to transform these absolute values into values which resemble the more familiar Pauling values. For ionization energies and electron affinities in electronvolts,<sup>[9]</sup>

$$\chi = 0.187(E_i + E_{ea}) + 0.17$$

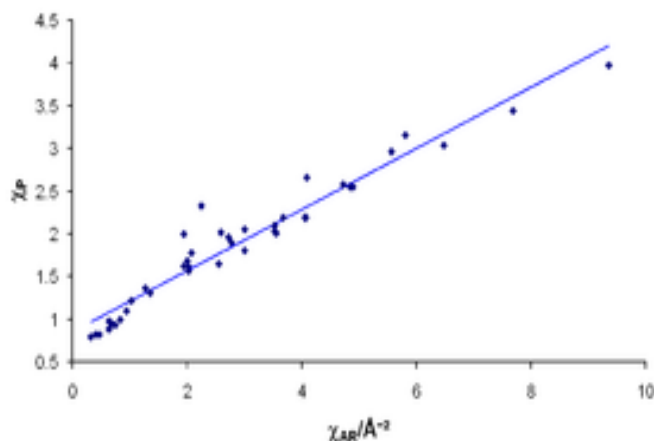
and for energies in kilojoules per mole,<sup>[10]</sup>

$$\chi = (1.97 \times 10^{-3})(E_i + E_{ea}) + 0.19.$$

The Mulliken electronegativity can only be calculated for an element for which the electron affinity is known, fifty-seven elements as of 2006. The Mulliken electronegativity of an atom is sometimes said to be the negative of the chemical potential. By inserting the energetic definitions of the ionization potential and electron affinity into the Mulliken electronegativity, it is possible to show that the Mulliken chemical potential is a finite difference approximation of the electronic energy with respect to the number of electrons., i.e.,  $\mu_{\text{Mulliken}} = -\chi_{\text{Mulliken}} = -(IP + EA)/2$

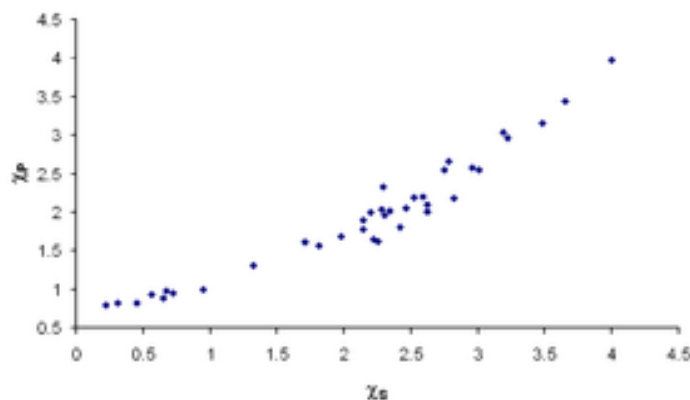
where IP and EA are the ionization potential and electron affinity of the atom, respectively.

## Allred–Rochow electronegativity



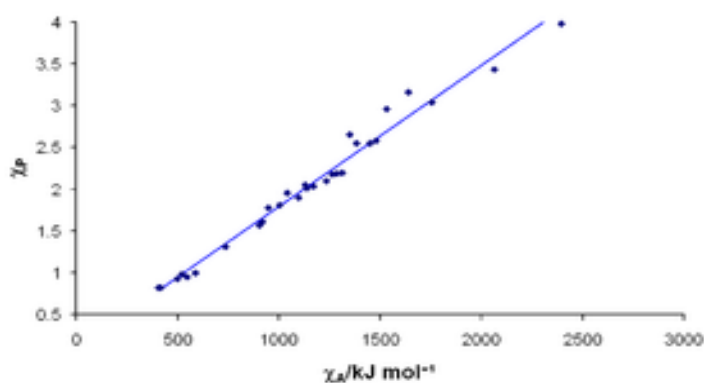
$$\chi = 0.359 \frac{Z^*}{r_{\text{cov}}^2} + 0.744.$$

## Sanderson electronegativity equalization



☞ The correlation between Sanderson electronegativities (x-axis, arbitrary units) and Pauling electronegativities (y-axis).

## Allen electronegativity



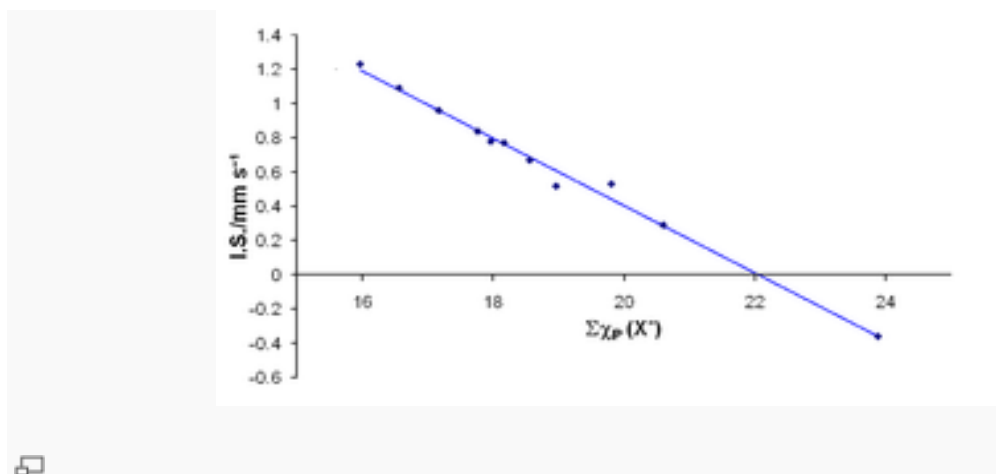
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The correlation between Allen electronegativities (x-axis, in kJ/mol) and Pauling electronegativities (y-axis).

$$\chi = \frac{n_s \varepsilon_s + n_p \varepsilon_p}{n_s + n_p}$$

where  $\varepsilon_{s,p}$  are the one-electron energies of s- and p-electrons in the free atom and  $n_{s,p}$  are the number of s- and p-electrons in the valence shell. It is usual to apply a scaling factor,  $1.75 \times 10^{-3}$  for energies expressed in kilojoules per mole or 0.169 for energies measured in electronvolts, to give values which are numerically similar to Pauling electronegativities.

## Correlation of electronegativity with other properties



The variation of the isomer shift (y-axis, in mm/s) of  $[\text{SnX}_6]^{2-}$  anions, as measured by  $^{119}\text{Sn}$  Mössbauer spectroscopy, against the sum of the Pauling electronegativities of the halide substituents (x-axis).

The wide variety of methods of calculation of electronegativities, which all give results which correlate well with one another, is one indication of the number of chemical properties which might be affected by electronegativity. The most obvious application of electronegativities is in the discussion of bond polarity, for which the concept was introduced by Pauling. In general, the greater the difference in electronegativity between two atoms, the more polar the bond that will be formed between them, with the atom having the higher electronegativity being at the negative end of the dipole. Pauling proposed an equation to relate "ionic character" of a bond to the difference in electronegativity of the two atoms,<sup>[3]</sup> although this has fallen somewhat into disuse.

Several correlations have been shown between infrared stretching frequencies of certain bonds and the electronegativities of the atoms involved:<sup>[20]</sup> however, this is not surprising as such stretching frequencies depend in part on bond strength, which enters into the calculation of Pauling electronegativities. More convincing are the

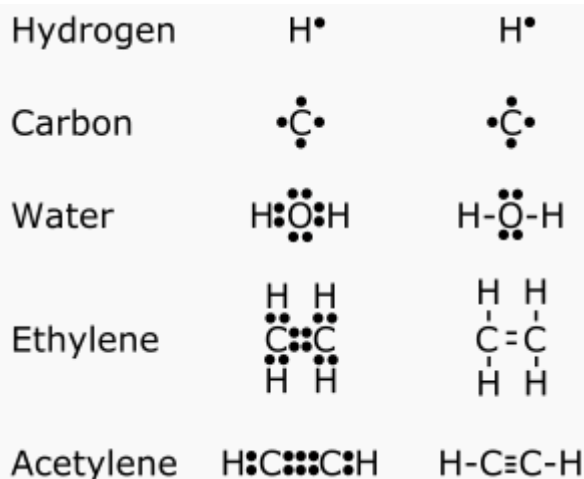
correlations between electronegativity and chemical shifts in NMR spectroscopy<sup>[21]</sup> or isomer shifts in Mössbauer spectroscopy<sup>[22]</sup> (see figure). Both these measurements depend on the s-electron density at the nucleus, and so are a good indication that the different measures of electronegativity really are describing "the ability of an atom in a molecule to attract electrons to itself".<sup>[1][3]</sup>

## Chemical bond

A **chemical bond** is an attraction between atoms that allows the formation of chemical substances that contain two or more atoms. The bond is caused by the electromagnetic force attraction between opposite charges, either between electrons and nuclei, or as the result of a dipole attraction. The strength of chemical bonds varies considerably; there are "strong bonds" such as covalent or ionic bonds and "weak bonds" such as dipole-dipole interactions, the London dispersion force and hydrogen bonding.

Since opposite charges attract via a simple electromagnetic force, the negatively charged electrons that are orbiting the nucleus and the positively charged protons in the nucleus attract each other. Also, an electron positioned between two nuclei will be attracted to both of them. Thus, the most stable configuration of nuclei and electrons is one in which the electrons spend more time *between* nuclei, than anywhere else in space. These electrons cause the nuclei to be attracted to each other, and this attraction results in the bond. However, this assembly cannot collapse to a size dictated by the volumes of these individual particles. Due to the matter wave nature of electrons and their smaller mass, they occupy a much larger amount of volume compared with the nuclei, and this volume occupied by the electrons keeps the atomic nuclei relatively far apart, as compared with the size of the nuclei themselves.

In general, strong chemical bonding is associated with the sharing or transfer of electrons between the participating atoms. The atoms in molecules, crystals, metals and diatomic gases— indeed most of the physical environment around us— are held together by chemical bonds, which dictate the structure and the bulk properties of matter.





Examples of Lewis dot-style chemical bonds between carbon *C*, hydrogen *H*, and oxygen *O*. Lewis dot depictions represent an early attempt to describe chemical bonding and are still widely used today.

## Overview of main types of chemical bonds

A chemical bond is an attraction between atoms. This attraction may be seen as the result of different behaviors of the outermost electrons of atoms. Although all of these behaviors merge into each other seamlessly in various bonding situations so that there is no clear line to be drawn between them, nevertheless behaviors of atoms become so qualitatively different as the character of the bond changes quantitatively, that it remains useful and customary to differentiate between the bonds that cause these different properties of condensed matter.

In the simplest view of a so-called 'covalent' bond, one or more electrons (often a pair of electrons) are drawn into the space between the two atomic nuclei. Here the negatively charged electrons are attracted to the positive charges of *both* nuclei, instead of just their own. This overcomes the repulsion between the two positively charged nuclei of the two atoms, and so this overwhelming attraction holds the two nuclei in a fixed configuration of equilibrium, even though they will still vibrate at equilibrium position. In summary, covalent bonding involves sharing of electrons in which the positively charged nuclei of two or more atoms simultaneously attract the negatively charged electrons that are being shared. In a polar covalent bond, one or more electrons are unequally shared between two nuclei. Covalent bonds often result formation of small collections of better-connected atoms called molecules, which in solids and liquids are bound to other molecules by forces that are often much weaker than the covalent bonds that hold the molecules internally together. Such weak intramolecular bonds give organic molecular substances, such as waxes and oils, their soft bulk character, and their low melting points (in which the molecules separate from each other). When covalent bonds link long chains of atoms in large molecules, however (polymers such as nylon), or when covalent bonds extend through networks though solids that are not composed of discrete molecules (such as diamond or quartz or the silicate minerals in many types of rock) then the structures that result may be both strong and tough (at least in the direction oriented correctly with networks of covalent bonds). Also, their melting points increase considerably.

In a simplified view of an *ionic* bond, the bonding electron is not shared at all, but transferred. In this type of bond, the outer atomic orbital of one atom has a vacancy which allows addition of one or more electrons. These newly added electrons potentially occupy a lower energy-state (effectively closer to more nuclear charge) than they experience in a different atom. Thus, one nucleus offers a more tightly bound position to an electron than does another nucleus, with the result that one

atom may transfer an electron to the other. This transfer causes one atom to assume a net positive charge, and the other to assume a net negative charge. The *bond* then results from electrostatic attraction between atoms, and the atoms become positive or negatively charged ions. Ionic bonds may be seen as extreme examples of polarization in covalent bonds. Ionic bonds are strong (and thus ionic substances require high temperatures to melt) but also brittle, since the forces between ions are short-range, and do not easily bridge cracks and fractures. This type of bond gives a characteristic physical character to mineral salt crystals, such as table salt and other classic mineral salts.

The last and rarely-mentioned type of bonding is *metallic* bond. In this type of bonding, each atom in a metal donates one or more electrons to a "sea" of electrons that reside between many metal atoms. In this sea, each electron is free (by virtue of its wave nature) to be associated with a great many atoms at once. The bond results because the metal atoms become somewhat positively charged due to loss of their electrons, while the electrons remain attracted to many atoms, without being part of any given atom. Metallic bonding may be seen as an extreme example of delocalization of electrons over a large system of covalent bonds, in which every atom participates. This type of bonding is often very strong (resulting in the tensile strength of metals). However, metallic bonds are more collective in nature than other types, and so at the same time they allow metal crystals to more easily deform because they are composed of atoms bound to each other and attracted to each other, but not in any particularly oriented ways. This results in the malleability of metals.

All bonds can be explained by quantum theory, but, in practice, simplification rules allow chemists to predict the strength, directionality, and polarity of bonds. The octet rule and VSEPR theory are two examples. More sophisticated theories are valence bond theory which includes orbital hybridization and resonance, and the linear combination of atomic orbitals molecular orbital method which includes ligand field theory. Electrostatics are used to describe bond polarities and the effects they have on chemical substances.

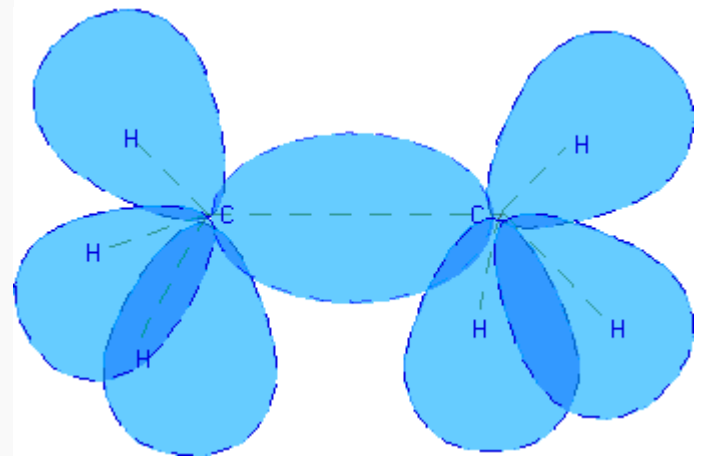
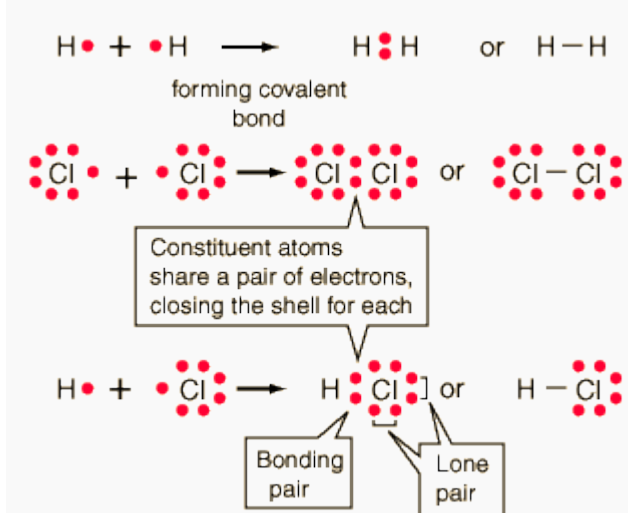
## Covalent bond

Covalent bonding is a common type of bonding, in which the electronegativity difference between the bonded atoms is small or nonexistent. Bonds within most [organic compound]s are described as covalent. See [sigma bond]s and pi bonds for LCAO-description of such bonding.

A polar covalent bond is a covalent bond with a significant ionic character. This means that the electrons are closer to one of the atoms than the other, creating an imbalance of charge. They occur as a bond between two atoms with moderately different electronegativities, and give rise to dipole-dipole interactions. The electronegativity of these bonds is 0.3 to 1.7 .

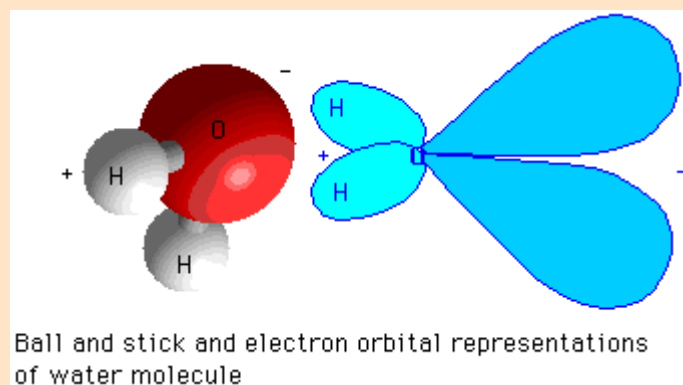
A coordinate covalent bond is one where both bonding electrons are from one of the atoms involved in the bond. These bonds give rise to Lewis acids and bases. The electrons are shared roughly equally between the atoms in contrast to ionic bonding. Such bonding occurs in molecules such as the ammonium ion ( $\text{NH}_4^+$ ) and are shown by an arrow pointing to the Lewis acid. Also known as non-polar covalent bond, the electronegativity of these bonds range from 0 to 0.3.

Molecules which are formed primarily from non-polar covalent bonds are often immiscible in water or other polar solvents, but much more soluble in non-polar solvents such as hexane



## Polar Covalent Bonds

Covalent bonds in which the sharing of the electron pair is unequal, with the electrons spending more time around the more nonmetallic atom, are called polar covalent bonds. In such a bond there is a charge separation with one atom being slightly more positive and the other more negative, i.e., the bond will produce a dipole moment. The ability of an atom to attract electrons in the presence of another atom is a measurable property called electronegativity.

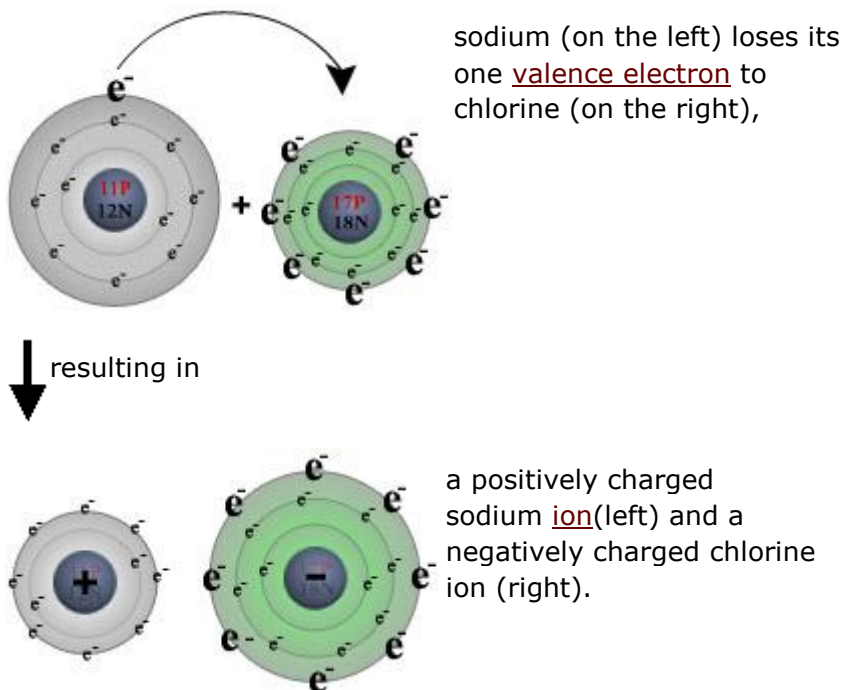
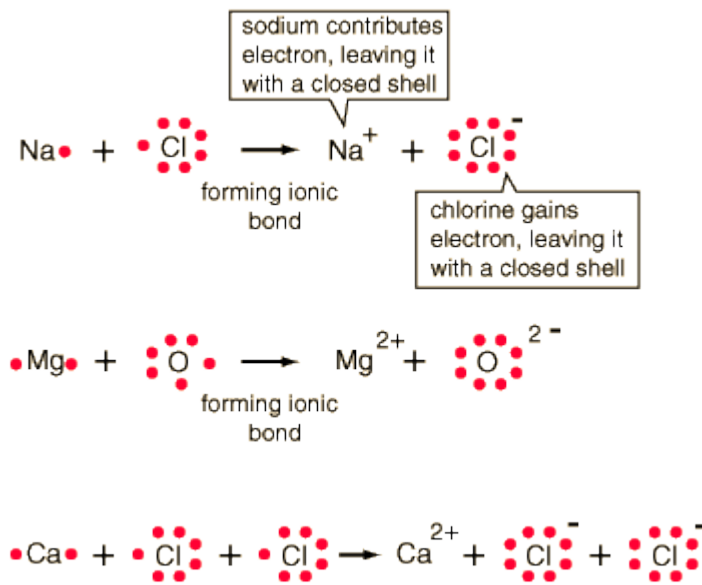


## Ionic bond

Ionic bonding is a type of electrostatic interaction between atoms which have a large electronegativity difference. There is no precise value that distinguishes ionic from covalent bonding, but a difference of electronegativity of over 1.7 is likely to be ionic, and a difference of less than 1.7 is likely to be covalent.<sup>[4]</sup> Ionic bonding leads to separate positive and negative ions. Ionic charges are commonly between  $-3e$  to  $+3e$ . Ionic bonding commonly occurs in metal salts such as sodium chloride (table salt). A typical feature of ionic bonds is that the species form into ionic crystals, in which no ion is specifically paired with any single other ion, in a specific directional bond. Rather, each species of ion is surrounded by ions of the opposite charge, and the spacing between it and each of the oppositely charged ions near it, is the same for all surrounding atoms of the same type. It is thus no longer possible to associate an ion with any specific other single ionized atom near it. This is a situation unlike that in covalent crystals, where covalent bonds between specific atoms are still discernable from the shorter distances between them, as measured by with such techniques as X-ray diffraction.

Ionic crystals may contain a mixture of covalent and ionic species, as for example salts of complex acids, such as sodium cyanide, NaCN. Many minerals are of this type. X-ray diffraction shows that in NaCN, for example, the bonds between sodium cations ( $\text{Na}^+$ ) and the cyanide anions ( $\text{CN}^-$ ) are *ionic*, with no sodium ion associated with any particular cyanide. However, the bonds between C and N atoms in cyanide are of the *covalent* type, making each of the carbon and nitrogen associated with *just one* of its opposite type, to which it is physically much closer than it is to other carbons or nitrogens in a sodium cyanide crystal.

When such salts dissolve into water, the ionic bonds are typically broken by the interaction with water, but the covalent bonds continue to hold. In solution, the cyanide ions, still bound together as single  $\text{CN}^-$  ions, move independently through the solution, as do sodium ions, as  $\text{Na}^+$ . These charged ions move apart because each of them are more strongly attracted to a number of water molecules, than to each other. The attraction between ions and water molecules in such solutions is due to a type of weak dipole-dipole type chemical bond.



### [The reaction of sodium with chlorine](#)

Concept simulation - Reenacts the reaction of sodium with chlorine.

## **Metallic bond**

In a metallic bond, bonding electrons are delocalized over a lattice of atoms. By contrast, in ionic compounds, the locations of the binding electrons and their charges are static. The freely-moving or delocalization of bonding electrons leads to classical metallic properties such as shininess (surface light reflectivity), electrical and thermal conductivity, ductility, and high tensile strength.

## **Hydrogen Bonding**

Hydrogen bonding differs from other uses of the word "bond" since it is a force of attraction between a hydrogen atom in one molecule and a small atom of high electronegativity in another molecule. That is, it is an intermolecular force, not an intramolecular force as in the common use of the word bond.

When hydrogen atoms are joined in a polar covalent bond with a small atom of high electronegativity such as O, F or N, the partial positive charge on the hydrogen is highly concentrated because of its small size. If the hydrogen is close to another oxygen, fluorine or nitrogen in another molecule, then there is a force of attraction termed a dipole-dipole interaction. This attraction or "hydrogen bond" can have about 5% to 10% of the strength of a covalent bond.

Hydrogen bonding has a very important effect on the properties of water and ice. Hydrogen bonding is also very important in proteins and nucleic acids and therefore in life processes. The "unzipping" of DNA is a breaking of hydrogen bonds which help hold the two strands of the double helix together.

## **Summary: electrons in chemical bonds**

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In the (unrealistic) limit of "pure" ionic bonding, electrons are perfectly localized on one of the two atoms in the bond. Such bonds can be understood by classical physics. The forces between the atoms are characterized by isotropic continuum electrostatic potentials. Their magnitude is in simple proportion to the charge difference.

Covalent bonds are better understood by valence bond theory or molecular orbital theory. The properties of the atoms involved can be understood using concepts such as oxidation number. The electron density within a bond is not assigned to individual atoms, but is instead delocalized between atoms. In valence bond theory, the two electrons on the two atoms are coupled together with the bond strength depending on the overlap between them. In molecular orbital theory, the linear combination of atomic orbitals (LCAO) helps describe the delocalized molecular orbital structures and energies based on the atomic orbitals of the atoms they came from. Unlike pure ionic bonds, covalent bonds may have directed anisotropic properties. These may have their own names, such as sigma bond and pi bond.

In the general case, atoms form bonds that are intermediates between ionic and covalent, depending on the relative electronegativity of the atoms involved. This type of bond is sometimes called polar covalent.

## **Valence bond theory**

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In 1927, valence bond theory was formulated and it argues that a chemical bond forms when two valence electrons, in their respective atomic orbitals, work or

function to hold two nuclei together, by virtue of effects of lowering system energies. Building on this theory, the chemist Linus Pauling published in 1931 what some consider one of the most important papers in the history of chemistry: "On the Nature of the Chemical Bond". In this paper, elaborating on the works of Lewis, and the valence bond theory (VB) of Heitler and London, and his own earlier works, Pauling presented six rules for the shared electron bond, the first three of which were already generally known:

1. The electron-pair bond forms through the interaction of an unpaired electron on each of two atoms.
2. The spins of the electrons have to be opposed.
3. Once paired, the two electrons cannot take part in additional bonds.

His last three rules were new:

4. The electron-exchange terms for the bond involves only one wave function from each atom.
5. The available electrons in the lowest energy level form the strongest bonds.
6. Of two orbitals in an atom, the one that can overlap the most with an orbital from another atom will form the strongest bond, and this bond will tend to lie in the direction of the concentrated orbital.

Building on this article, Pauling's 1939 textbook: *On the Nature of the Chemical Bond* would become what some have called the "Bible" of modern chemistry. This book helped experimental chemists to understand the impact of quantum theory on chemistry. However, the later edition in 1959 failed to adequately address the problems that appeared to be better understood by molecular orbital theory. The impact of valence theory declined during the 1960s and 1970s as molecular orbital theory grew in usefulness as it was implemented in large digital computer programs. Since the 1980s, the more difficult problems of implementing valence bond theory into computer programs have been solved largely, and valence bond theory has seen a resurgence.

## **Comparison of valence bond and molecular orbital theory**

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In some respects valence bond theory is superior to molecular orbital theory. When applied to the simplest two-electron molecule,  $H_2$ , valence bond theory, even at the simplest Heitler-London approach, gives a much closer approximation to the bond energy, and it provides a much more accurate representation of the behavior of the electrons as chemical bonds are formed and broken. In contrast simple molecular orbital theory predicts that the hydrogen molecule dissociates into a linear superposition of hydrogen atoms and positive and negative hydrogen ions, a completely unphysical result. This explains in part why the curve of total energy against interatomic distance for the valence bond method lies above the curve for the

molecular orbital method at all distances and most particularly so for large distances. This situation arises for all homonuclear diatomic molecules and is particularly a problem for  $F_2$ , where the minimum energy of the curve with molecular orbital theory is still higher in energy than the energy of two F atoms.

The concepts of hybridization are so versatile, and the variability in bonding in most organic compounds is so modest, that valence bond theory remains an integral part of the vocabulary of organic chemistry. However, the work of Friedrich Hund, Robert Mulliken, and Gerhard Herzberg showed that molecular orbital theory provided a more appropriate description of the spectroscopic, ionization and magnetic properties of molecules. The deficiencies of valence bond theory became apparent when hypervalent molecules (e.g.  $PF_5$ ) were explained without the use of d orbitals that were crucial to the bonding hybridisation scheme proposed for such molecules by Pauling. Metal complexes and electron deficient compounds (e.g. diborane) also appeared to be well described by molecular orbital theory, although valence bond descriptions have been made.

In the 1930s the two methods strongly competed until it was realised that they are both approximations to a better theory. If we take the simple valence bond structure and mix in all possible covalent and ionic structures arising from a particular set of atomic orbitals, we reach what is called the full configuration interaction wave function. If we take the simple molecular orbital description of the ground state and combine that function with the functions describing all possible excited states using unoccupied orbitals arising from the same set of atomic orbitals, we also reach the full configuration interaction wavefunction. It can be then seen that the simple molecular orbital approach gives too much weight to the ionic structures, while the simple valence bond approach gives too little. This can also be described as saying that the molecular orbital approach is too *delocalised*, while the valence bond approach is too *localised*.

The two approaches are now regarded as complementary, each providing its own insights into the problem of chemical bonding. Modern calculations in quantum chemistry usually start from (but ultimately go far beyond) a molecular orbital rather than a valence bond approach, not because of any intrinsic superiority in the former but rather because the MO approach is more readily adapted to numerical computations. However better valence bond programs are now available.